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AB-INITIO MOLECULAR DYNAMICS SIMULATIONS OF MOLTEM Ni-BASED SUPERALLOYS (PREPRINT)

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14. ABSTRACT
Convective instabilities responsible for misoriented grains (freckle defects) in directionally solidified turbine airfoils are produced by variations in liquid–metal density with composition and temperature across the solidification zone. Here, fundamental properties of molten Ni-based alloys, required for modeling these instabilities, are calculated using ab initio molecular dynamics simulations. Previous calculations on elemental, binary and ternary alloys produced liquid-phase molar volumes (V(c,T)) within 0.6-1.8% of available experimental data and demonstrated that the simulations cells of 500 atoms were sufficient to converge properties of interest. In this work density inversion, an increase in density with increasing temperature is assessed in model Ni-Al-W and RENE-N4 alloys. Calculations are performed using a recently implemented constant pressure methodology (NPT) which enables efficient simulation of highly complex alloys. Density inversion (~2%) is found for the Ni-Al-W alloys for target compositions and temperatures consistent with 0 and 0.5 solid volume fractions in the melt.

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Ab-Initio Molecular Dynamics Simulations of Molten Ni-Based Superalloys

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Abstract

Convective instabilities responsible for misoriented grains (freckle defects) in directionally solidified turbine airfoils are produced by variations in liquid–metal density with composition and temperature across the solidification zone. Here, fundamental properties of molten Ni-based alloys, required for modeling these instabilities, are calculated using ab initio molecular dynamics simulations. Previous calculations on elemental, binary and ternary alloys produced liquid-phase molar volumes (V(c,T)) within 0.6-1.8% of available experimental data and demonstrated that the simulations cells of 500 atoms were sufficient to converge properties of interest. In this work density inversion, an increase in density with increasing temperature is assessed in model Ni-Al-W and RENE-N4 alloys. Calculations are performed using a recently implemented constant pressure methodology (NPT) which enables efficient simulation of highly complex alloys. Density inversion (~2%) is found for the Ni-Al-W alloys for target compositions and temperatures consistent with 0 and 0.5 solid volume fractions in the melt. Recently published parameterizations of V(c,T) developed using binary experimental data from a narrow range of compositions do not predict the expected density inversion. The liquid metal density for a Ni based superalloy, RENE-N4, is calculated at the liquidus and solidus temperatures expected in the solidification (mushy) zone. Multiple 500 atom instantiations of the superalloy melt produce densities well within expected numerical error. This illustrates that simulations of moderate spatial and temporal scales sample enough degrees of freedom to properly represent the configuration entropy found in a liquid metal superalloy.

1. Introduction

Over the last decade alloy developers have increased the concentration of refractory elements in single crystal Ni-based superalloys in order to improve the balance of high temperature properties. Unfortunately, higher concentrations of some of these elements are associated the formation of defects during the directional solidification process. These so-called freckle defects are formed by enhancing density-driven convective instabilities in the solidification front (i.e., the mushy zone) and consist of chains of small equiaxed grains. The high-angle grain boundaries and composition gradients associated with freckles are known to severely degrade turbine airfoil performance. A systems design of the processing-structure-properties relationship for these alloys requires a quantitative model for predicting processing regimes which will allow defects-free commercial castings over the widest possible range of refractory metal compositions. Such casting defects form due to thermo-solutal convection in the mushy zone, and current theory indicates such instabilities are likely when a critical Rayleigh number is exceeded.[1–4] The Rayleigh number (R) is a measure of the ratio of the buoyancy force to the retarding frictional force in the mushy zone:

$$R = \left(\Delta\rho / \bar{\rho}\right) gKl / \alpha v \tag{1}$$

where l is an appropriate length scale, K is the average permeability, g gravitational acceleration, α is the thermal diffusivity, v is the kinematic viscosity of the fluid, and $\left(\Delta\rho / \bar{\rho}\right)$, the density contrast, is a measure of the density variation over the mushy zone between the solid and liquid phases. The tendency towards defect formation is highly sensitive to the permeability of the mushy zone (e.g., the primary dendrite arm spacing) as well as the density contrast. Historically, models for the Rayleigh- number criterion for freckle formation assume that the density gradients are aligned with both the solidification front and gravity. However, this assumption has become problematic as turbine airfoil geometries have

become more complex with the introduction of cooling channels and other design features. Currently, most castings have significant heat losses through the mold that create horizontal thermal gradients and tilted solid-liquid interfaces.

Validating mathematical models for freckle formation in specific alloy systems requires accurate assessment of the various parameters in Eq. 1. The permeability and density gradients are probably the most poorly documented quantities for superalloys. Values for the former quantities have recently been assessed using fluid-flow simulations employing realistic models for the mushy-zone topology obtained from three-dimensional reconstructions derived by serial sectioning.[5] The focus of these high performance computing Challenge calculations is the development and validation of accurate models for $\Delta\rho$ by *ab initio* molecular dynamics (AIMD) simulations. Here $\Delta\rho$ represents the mass-density difference between the hot liquid near the dendritic solid-liquid interface and the cooler melt at the top and side-walls of the casting. The mass-density difference originates from both the composition (c) and temperature (T) dependencies of the liquid-phase molar volume $V(c,T)$.

Recently, Mukai et al.[6–8] developed a multi-component parameterization for $V(c,T)$ in superalloys based on extensive experimental measurements of the densities of binary liquid Ni alloys, and a few representative ternaries.[8] Intrinsic to this interaction scheme is the assumption that the partial molar volume of each solute species is independent of the compositions of the others. Therefore, effects arising from the interactions between different solute species atoms are ignored. Also, due to the limited availability of measured density data several key elements such as Re treated as parameters in fits to $V(c,T)$ data for multicomponent superalloys. While Mukai's parameterizations are within a few percent of the measured values for the liquid metal densities of several superalloys, we are unaware of experimental data for the composition and temperature dependent densities in the multicomponent superalloy RENE-N4. In the current work we are using of state-of-the-art AIMD simulations as a means for testing the accuracy of the model for parameterizing $\rho(c,T)$ in this system. These calculations are also being used to independently test the accuracy of the Mukai parameters for elements where direct measurements of liquid density are unavailable.

2. Method

Ab-initio molecular dynamic simulations, based on density functional theory (DFT), have been used to evaluate the properties of molten Ni-based alloys. Ionic positions were evolved in time using classical Nosé-Hoover dynamics[9,10], for both a fixed-number, volume, and temperature (NVT) and fixed-number, pressure and temperature (NPT) ensembles. The time evolution was based on inter-atomic forces (i.e. the Hellmann-Feynman forces) computed directly from DFT using the commercial DFT software VASP (Vienna ab-initio simulation package)[11–14], developed at the Institut für Materialphysik of the Univerität Wien. As we have shown previously the VASP code scales well for systems with large numbers of atoms on parallel computers with high-bandwidth communications networks.[15] The underlying algorithms employed in VASP have been extensively tested and optimized for parallel processing with large numbers of processors.

Previously we have used NVT dynamics to calculate the molar volumes of a variety of simple, binary and ternary metal alloys.[16] These include Ni, Al, Ni-X, and Ni-Al-X (X= W, Re, Ta) alloys at several compositions and temperatures. The DFT calculations made use of ultrasoft pseudo potentials[17,18] and the PW91 generalized-gradient approximation (GGA)[19] with a plane-wave basis cutoff energy of 260 eV. The simulations employ a single k-point (Γ) and time steps (Δt) for the MD simulations were chosen as Δt=0.002 ps or Δt=0.003 ps, to ensure that the conserved energy in the Nosé-Hoover dynamics displayed a drift in time no larger than 1 meV/atom·ps. Analysis radial distribution functions suggest that the simulation system sizes are large enough to avoid introducing of appreciable order in the liquid structures. Total simulation times ranged from 5–10ps, a time interval long enough to obtain good statistical precision in calculated molar volumes and diffusion rates.[16]

In order to improve the efficiency of the calculations the current version of VASP (release 4.5) was modified to integrate the molecular dynamics equations appropriate for fixed number, pressure, and temperature ensemble using the *ab initio* computed forces and pressures. The implementation allows for Parrinello-Rahman dynamics using (deterministic) Nosé-Hoover chain thermostats for the atoms and the simulation cell vectors or Parrinello-Rahman dynamics using Langevin thermostats with stochastic forces and pressure tensors. The dynamics are constrained to eliminate center-of-mass motion and to impose irrotational deformations on the simulation cell and a further option restricts deformations to volumetric (shape-preserving) fluctuations. Minimal changes were made to the VASP source code to include this new AIMD option and to accommodate the required input and output parameters.[16]

Current calculations are focused on known freckle prone alloys these include model Ni-Al-W and the Ni-based superalloy RENE-N4. Assuming that other parameters for the Rayleigh criteria are constant across the mushy zone, the signature for freckle formation is reduced to the condition when the liquid metal at higher temperature has a greater density than at lower temperatures. Convective flow is then highly favored as the high temperature liquid at the top of the mushy

zone displaces the lower temperature liquid at the bottom of the mushy zone. It is precisely this instability that produces convective flow during directional solidification. Density inversion is more complex than just a negative coefficient of thermal expansion, because the (equilibrium) composition of the liquid changes with temperature across the height of the mushy zone. Also, there is some ambiguity about the relevant temperature range sampled in the mushy zone.

For the model Ni-Al-W alloy we adopted a nominal composition of Ni-14Al-3W at% and evaluated the equilibrium liquid compositions and temperatures for 0 and 0.5 solid volume fraction using CalPhad (Pandat™) methods to estimate the Scheil solidification pathway.[17] The predicted liquid compositions at 1711 and 1720 K are Ni82-Al15.6-W2.4 and Ni83-Al14-W3 at % respectively. For the 500 atom AIMD cells this corresponds to $Ni_{410}Al_{78}W_{12}$ and $Ni_{415}Al_{70}W_{15}$ where the subscripts refer to the number of atoms of each element in the cell. For RENE-N4 we adopted the solidus and liquidus as the reference states. Using a similar Scheil model for RENE-N4, the solidus and liquidus temperatures were used to calculate the approximate liquid compositions at the bottom and top of the solidification zone.[18] The predicted compositions are Ni62.2-Cr11.0-Co5.2Mo1.3-W1.9-Al10.-Ti5.8-Ta2.3-Nb0.5 and Ni63.0-Cr11.2-Co7.6-Mo0.9-W1.9-Al9.2-Ti4.3-Ta1.6-Nb0.3 at 1,635K and 1,582K respectively. These chemistries include very dilute Nb additions which were removed from the calculations, the balance in composition being spread proportionally overall the remaining species. These compositions then yield the following number of atoms of each species in the 500 atom cell calculations: $Ni_{315}Cr_{56}Co_{38}Mo_5W_{10}Al_{46}Ti_{22}Ta_8$ and $Ni_{312}Cr_{55}Co_{26}Mo_6W_{10}Al_{50}Ti_{29}Ta_{12}$ for 1,635K and 1,582K respectively. These chemistries were then used to construct 500 atom cells with random distributions of the appropriate elements. The different instantiations at each temperature were run in order to assess the influence of configurational entropy on the molar volume or alloy density.

The NPT density inversion calculations for model and Ni-based superalloys make use of PAW (Projector Augmented Wave) and the PW91 generalized-gradient approximation (GGA).[19] This was found to produce a good representation of the liquid metal superalloy.[16] Improvements in the electron-ion interactions require a larger cutoff energy for the planewave basis representing the electronic wavefunctions. However, the NPT dynamics allow derivation of the equilibrium volume in a single series of calculations, significantly reducing the required computational effort.

3. Results and Analysis

The main focus of these AIMD simulations is to demonstrate that such methods can reliable predict liquid metal densities to a level of accuracy that can inform models convective instabilities. Table 1 shows the calculated density at the 0 and 0.5 volume fraction temperatures for a nominal composition of Ni-14Al-3W at%. This alloy was chosen because it has been demonstrated to produce freckle defects in conventional Bridgeman directional solidification. Here the results are given as a density for the two solid volume fractions. The AIMD calculations predict a 2% increase in the density going from 1711 to 1720K which suggests a relatively strong density inversion. Further, there is also a decrease in the molar volume with increasing temperature, from 7.782(5) to 7.767(8) cm^3/mole, so density inversion is predicted even when the increase in elemental mass is not taken into account (i.e. the change in composition from the Scheil model favors an increase in density at the higher temperature). When the Mukai parameterization is applied to the model alloy the liquid metal density is essentially identical (within statistical error), so no density inversion would be expected.

The Ni-based superalloys have extremely complex alloy chemistries, and RENE-N4 is no exception. The first goal is to show that a relatively small population of atoms, in this case 500 atoms, can give a precise and reproducible density in molecular dynamics simulations running for less than ~7 ps. Table 2 shows the AIMD predicted densities for four different instantiations (at the solidus and liquidus temperatures) of 500 atom simulation with runtimes less than 8 ps. For the eight cases considered the AIMD densities are self-consistent and highly reproducible. The results illustrate that even for very complex chemistries, liquid metals densities can be accurately calculated using relatively small simulation cells.

Table 1. Predicted liquid metal densities for the Ni-Al-W model system. The numbers in parentheses represent the expected error on the last digit. For the AIMD results this is the estimated 95% confidence interval generated through standard propagation of error. For Mukai's parameterization expected error is taken to be within 2.5%.[8]

V_f	T (K)	Composition	Density (g/cm^3)	
		Atomic (/500)	AIMD	Mukai
0	1720	$Ni_{415}Al_{70}W_{15}$	7.46(2)	7.8(2)
0.5	1711	$Ni_{410}Al_{78}W_{12}$	7.29(1)	7.8(2)

The calculated densities for RENE-N4, shown in Table 2, do not predict a density inversion at these temperatures and compositions. Similar to the results for the model alloy, Mukai's parameterization produces numerically equivalent densities for the liquidus and solidus states. Given the success in applying the 0-0.5 solid volume fraction reference states in the Ni-Al-W

model system it is possible that the liquidus and solidus compositions of RENE-N4 are not representative of the relevant liquid metal densities responsible for convective instability. Fortunately, the current results show that the new reference states can be accurately represented with several moderate sized calculations. Calculations for 0.0-0.5 solid volume fractions in RENE-N4 are underway.

Table 2. AIMD predicted densities (g/cm^3) for RENE-N4 at the Scheil model solidus and liquidus temperatures and compositions. Numbers in parentheses are the expected errors as defined in Table 1.

Temperature		1582 K	1625 K
Composition		$Ni_{315}Cr_{56}Co_{38}Mo_5W_{10}Al_{46}Ti_{22}Ta_8$	$Ni_{312}Cr_{55}Co_{26}Mo_6W_{10}Al_{50}Ti_{29}Ta_{12}$
Density (g/cm^3)	AIMD-1	7.72(2)	7.51(2)
	AIMD-2	7.73(2)	7.51(2)
	AIMD-3	7.73(2)	7.51(2)
	AIMD-4	7.72(2)	7.51(2)
	Mukai[8]	7.3(2)	7.3(2)

4. Summary

AIMD simulations have been performed to derive liquid-phase densities for model Ni-Al-W ternary alloy compositions designed to produce convective instabilities through a density inversion. Similarly, a freckle defect prone Ni-based superalloy, RENE-N4, were studied using four AIMD instantiations at the liquidus and solidus temperatures. The current AIMD calculations for the model ternary Ni-Al-W alloy predicts a 2% density inversion, consistent with convective instabilities that produce freckle defects. For the RENE-N4 superalloy a series of moderately sized simulation cells (i.e. 500 atoms) based on random distributions of the atomic species produced numerically equivalent results. This suggests that even for highly complex chemistries moderately sized AIMD simulations can produce reliable results. Finally, results for RENE-N4 indicate that reference chemistries and temperature based on 0.0-0.5 solid volume fraction may produce liquid metal densities more relevant to convective instabilities .

Future work will involve more RENE-N4 AIMD calculations and application these methods to a larger set of Ni-based superalloys, particularly those that are know to form solidification defects. Also, in the coming year we will begin to apply methods for predicting the shear viscosity in simple and binary alloys. The shear viscosity is another parameter in the Rayleigh-number criteria (eq. 1) that is difficult to measure, and is not well known for complex alloys. Finally, we will run alloy compositions for several other Ni-based superalloys where there are reliable, though limited, experimental measurements of liquid metal densities.

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